Application No. 09/909,288 Reply Date July 2, 2004 Reply to Official Action (Paper No. 12) of April 2, 2004

# REMARKS/ARGUMENTS Status Of The Claims

The First Official Action dated April 2, 2004, has been carefully considered. Reconsideration and allowance of all claims is respectfully requested. Claims 38-66 remain in the application for consideration.

#### **Formal Matters**

Claims 1-29 and 36 were previously rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over Claims 14-23 and 32-37 of U.S. Patent Application Serial No. 10/253,113, Claims 31-32 of U.S. Patent Application Serial No. 09/909,233, Claims 22-23 of U.S. Patent Application Serial No. 10/109,344, Claim 77 of U.S. Patent Application Serial No. 09/909,403 and Claim 80 of U.S. Patent Application Serial No. 09/910,281 have been withdrawn.

# Rejections Under 35 U.S.C. § 103(a)

A. Claims 38-51, 53-55, and 58-66 were rejected under 35 U.S.C. § 103(a) as being unpatentable over the Culshaw et al U.S. Patent 5,202,050 (hereinafter referred to as "Culshaw et al") in view of Japanese reference JP 8-151597 (hereinafter referred to as "JP '597").

The Examiner asserted that Culshaw et al disclose hard surface cleaning compositions which contain a binary mixture of an organic solvent and a narrowly defined chelating agent with a pH of generally in the range of from 5 to 11, but that Culshaw et al fail to teach adding particles of smectite clay having a platelet size of less than 100 nm or a cleaning composition having the specific physical parameters containing a soil swelling agent, a smectite clay with a particle size of less than 100 nm, and other requisite components of the composition recited in the claims. The Examiner also asserted that the broad teachings of Culshaw et al would encompass compositions having the same flow viscosity, shear thinning properties, and other physical parameters as set forth by the claims. The Examiner further alleged that the deficiencies of Culshaw et al are taught by JP '597, which the Examiner asserted discloses a liquid detergent composition containing a clay mineral having an average particle diameter of 10 to 5000 nm and anionic and nonionic surfactants.

However, as will be set forth in detail below, it is submitted that the hard surface cleaning compositions as defined by Claims 38-51, 53-55, and 58-66 are non-obvious over and patentably distinguishable from Culshaw et al in view of JP '597. Accordingly, this rejection is traversed and

Application No. 09/909,288 Reply Date July 2, 2004 Reply to Official Action (Paper No. 12) of April 2, 2004

reconsideration is respectfully requested.

The hard surface cleaning compositions defined by independent Claims 38, 59, and 66 are advantageous in that they sufficiently low viscosity to allow application by spraying, while they also exhibit sufficiently low flow velocity to avoid runoff from surfaces to which they are applied. This cleaning composition comprises the combination of a soil swelling agent and a thickening system, and has a pH, as measured in a 10% solution in distilled water, from greater than 11 to about 14.

It is well settled that to support a rejection under 35 U.S.C. § 103, a reference must provide an enabling disclosure, i.e., it must place the claimed invention in the possession of the public. *In re Payne*, 203 U.S.P.Q. 245 (CCPA 1979). The combination of Culshaw et al and JP '597 does not result in the hard surface cleaning composition of Claims 38-51, 53-55, and 58-66.

Culshaw et al disclose a cleaning composition containing a binary mixture of an organic solvent and a narrowly defined organic chelating agent, and a pH from about 5 to about 11 (col. 7, lines 53-55). Applicants find no teaching, suggestion or motivation, in Culshaw et al. relating to hard surface cleaning compositions comprising a soil swelling agent in combination with a thickening system, having a pH, as measured in a 10% solution in distilled water, from greater than 11 to about 14, as defined in Claims 38, 59, and 66.

JP '597 discloses a liquid detergent composition containing a clay mineral having an average particle diameter of 10 to 5000 nm and anionic and nonionic surfactants. JP'597 does not resolve the deficiencies of Culshaw et al with respect to the pH limitations. Moreover, Culshaw et al in combination with JP '597 does not render the limitations of Claims 38-51, 53-55, and 58-66 obvious as well. Rather, there is a teaching away from the claimed pH range. Culshaw et al teach a pH from about 5 to about 11, while JP '597 mentions a pH range from 5-6 (see JP '597 page 3, paragraph 0014, lines 44-45), each of which lies outside the pH range of the present claims.

Obviousness is tested by "what the combined teachings of the references would have suggested to those of ordinary skill in the art." *In re Keller*, 642 F.2d 413, 425, 208 U.S.P.Q. 871, 881 (CCPA 1981). But it "cannot be established by combining the teachings of the prior art to produce the claimed invention, absent some teaching or suggestion supporting the combination." *ACS Hosp. Sys., Inc. v. Montefiore Hosp. et al*, 732 F.2d 1572, 1577, 221 U.S.P.Q. 929, 933 (Fed. Cir. 1984). And "teachings of references can be combined only if there is some suggestion or incentive to do so." Id. Therefore, "when determining the patentability of a claimed invention which combines two known elements, 'the question is whether there is something in the prior art as a whole to suggest the desirability, and thus the obviousness, of making the combination." *In re Beattie*, 974 F.2d 1309, 1311-12, 24 U.S.P.Q.2d (BNA) 1040, 1042 (Fed. Cir. 1992) (quoting *Lindemann*, 730 F.2d at 1462, 221 U.S.P.Q. (BNA) at 488). Since Culshaw et al and JP '597 do

not teach or suggest a composition having a pH, as measured in a 10% solution in distilled water, from greater than 11 to about 14, as defined by Claim 38, there can be no expectation of success. As such, Culshaw et al in view of JP '597 does not render Claims 38, 59, and 66, and their dependent claims, obvious.

It is therefore submitted that the cleaning compositions as defined by Claims 38-51, 53-55, and 58-66 are non-obvious over and patentably distinguishable from Culshaw et al in combination with JP '597 and the rejection of Claims 38-51, 53-55, and 58-66 under 35 U.S.C. § 103(a) has been overcome. Reconsideration is respectfully requested.

# B. Claims 38-55 and 57-66 were rejected under 35 U.S.C. § 103(a) as being unpatentable over the Feng U.S. Patent 5,929,007 (hereinafter referred to as "Feng") in view of Culshaw et al and JP '597.

The Examiner asserted that Feng discloses an aqueous hard surface cleaning composition wherein the composition includes an amine oxide, chelating agent, caustic component, and a glycol ether solvent system having one glycol ether or glycol ether acetate solvent. The Examiner also asserted that the broad teachings of Feng in combination with Culshaw et al and JP '597 would encompass compositions having the same flow viscosity, shear thinning properties, and other physical parameters as set forth by the Claims. The Examiner further alleged that the deficiencies of Feng are taught by JP '597, asserting that JP '597 discloses a liquid detergent composition containing a clay mineral having an average particle diameter of 10 to 5000 nm and anionic and nonionic surfactants.

However, as will be set forth in detail below, it is submitted that the hard surface cleaning compositions as defined by Claims 38-55 and 57-66 are non-obvious over and patentably distinguishable from Feng in view of Culshaw et al and JP '597. Accordingly, this rejection is traversed and reconsideration is respectfully requested.

The Applicants bring to the Examiner's attention that when prior-art references require a selective combination to render obvious a subsequent invention, there must be some reason for the combination other than the hindsight-gleaned form the invention itself. *Uniroyal Inc. v. Rudkin-Wiley Corp.*, 837 F.2d 1044, 5 U.S.P.Q.2d 1434 (Fed. Cir. 1988). In other words, the invention must have been obvious at the time it was made; the Examiner cannot use hindsight to reconstruct the invention from the prior art and say the invention was obvious, *W.L. Gore, 721 F.2d at 1553.* To establish prima facie obviousness of the claimed invention, all the claim limitations must be taught or suggested by the prior art, *In re Royka*, 490 F.2d 981, 180 U.S.P.Q. 580 (CCPA 1974). As recited above, obviousness is tested by "what the combined teachings of the references would have suggested to those of ordinary skill in the art." *In re Keller*, supra; see also *Leinoff v. Louis Milona & Sons Inc.*, 726 F.2d 734, 739 (Fed. Cir. 1984). But it "cannot be

established by combining the teachings of the prior art to produce the claimed invention, absent some teaching or suggestion supporting the combination." ACS Hosp. Sys., Inc. v. Montefiore Hosp. et al, supra; see also Carella, 804 F.2d at 140. And "teachings of references can be combined only if there is some suggestion or incentive to do so." Id. Therefore, "when determining the patentability of a claimed invention which combines two known elements, 'the question is whether there is something in the prior art as a whole to suggest the desirability, and thus the obviousness, of making the combination." In re Beattie.

As noted above, the Examiner admits that Feng fails to teach a cleaning composition having particles with a platelet size of less than 100 nm or a cleaning composition having the specific physical parameters containing a soil swelling agent, a smectite clay with a particle size of less than 100 nm, and other requisite components of the composition, as recited in the claims. In fact, Feng teaches alkaline cleaning compositions having an overall pH at least about 11.5 or greater. The pH of Feng's preferred embodiment is desirably "about 13 and higher" (col. 3, lines 52-55).

The courts have ruled in the case of W.L. Gore & Associates, Inc. v. Garlock, Inc. 721 F.2d 1540, 220 USPQ 303 (Fed. Cir. 1983), cert. denied, 469 U.S. 851 (1984) that a prior art reference must be considered in its entirety, i.e., as a whole, including portions that would lead away from the claimed invention. The deficiencies of Feng with respect to Claims 38-55 and 57-66 are not resolved by either Culshaw et al or JP '597, alone or in combination. The Feng composition requires a 0.01-2.5% of a caustic component (col. 2, line 7), preferably sodium hydroxide (col. 4, lines 1-2). There is no such caustic component requirement in the any of the compositions of Culshaw et al or JP'597. Rather, Culshaw et al and JP'597 appear to be teaching away from highly alkaline cleaning compositions by disclosing a specific pH range or as a result of their silence as to the acceptability of a highly alkaline pH or the presence of alkalinzing agents. Specifically, there is no motivation in Culshaw et al or JP'597 to direct one skilled in the art to prepare cleaning compositions having a highly alkaline pH (i.e. greater than 11.5) using particles having a platelet size of less than 100 nm or a cleaning composition having the specific physical parameters containing a soil swelling agent, a smectite clay with a particle size of less than 100 nm, and other requisite components of the composition, as asserted by the Examiner. Thus, considering the entirety of Culshaw and JP '597, one skilled in the art would not look to reference combinations that are absent motivation to use pH ranges that do not overlap with Feng in preparing a cleaning composition according to the present claims.

By picking and choosing among individual elements of assorted parts of references, the Applicants submit that the Examiner has used hindsight to reconstruct the invention. Since, there is no motivation, suggestion or teaching in Feng, alone or in combination with Culshaw et al, or JP '597, of the desirability of practicing their inventions outside the disclosed pH range, there can

be no expectation of success. Thus, the Applicants do not believe that Feng in view of Culshaw et al and JP '597 renders independent Claims 38, 59, and 66, and their dependent claims, obvious.

It is therefore submitted that the cleaning compositions as defined by Claims 38-55 and 57-66 are non-obvious over and patentably distinguishable from Feng in combination with Culshaw et al and JP '597, and the rejection of Claims 38-55 and 57-66 under 35 U.S.C. § 103 has been overcome. Reconsideration is respectfully requested.

C. Claim 56 was rejected under 35 U.S.C. § 103(a) as being unpatentable over Culshaw et al. in view of JP '597 or Feng in view of Culshaw et al. and JP '597 as applied to the rejection of Claim 38, from which Claim 56 depends, and further in view of the Ofosu-Asante U.S. Patent 5,739,092 (hereinafter referred to as "Ofosu-Asante").

The Examiner admitted that none of the previously cited references taught the use of a divalent cation in addition to the other requisite components of the composition as recited in Claim 56. The Examiner relied on Ofosu-Asante as teaching a liquid or gel dishwashing detergent composition containing alkyl ethoxy carboxylate surfactant and calcium or magnesium ions, and that the presence of such calcium or magnesium ions can improve the cleaning of greasy soils for compositions, manifest mildness to the skin, and provide good storage stability.

However, as will be set forth in detail below, it is submitted that the hard surface cleaning composition as defined by Claim 56 is non-obvious over and patentably distinguishable from Culshaw et al, Feng and JP '597 in view of Ofosu-Asante. Accordingly, this rejection is traversed and reconsideration is respectfully requested.

The deficiencies of Culshaw et al, Feng and JP '597 are not resolved by Ofosu-Asante. Moreover, Culshaw et al, Feng and JP '597 in combination with Ofosu-Asante do not render the limitations of Claim 56 obvious. Ofosu-Asante broadly discloses a light-duty dishwashing detergent composition generally having a alkyl ethoxy surfactant, calcium or magnesium ions, and an alkylpolyethoxypolycarboxylate surfactant (col. 6, lines 60-65), having a pH range of from 7 to 11 (col. 5, lines 41-49), with a preferred pH range from 8.5 to 9.5. Ofosu-Asante caution that "at the upper pH range, i.e. between about 10 and 11, compositions containing magnesium ions readily form hydroxide precipitates" (col. 6, lines 62-65; see also col. 7, lines 1-4). Thus, there is a teaching away from the claimed pH range. Though the Applicants' composition may contain alkylpolyethoxypolycarboxylate surfactant and divalent cations, the Examiner cannot pick and choose among individual elements of assorted parts of references to recreate the claimed invention. The Examiner has some burden to show some teaching or suggestion in references and to support their use in the particular claimed combinations. *Smith-Kline Diagnostics, Inc. v. Helena Laboratories, Corp.*, 8 U.S.P.Q.2d 1468, 1475 (Fed. Cir. 1988) (citation omitted). The Applicants find no teaching or suggestion in any of these references relating to hard surface

cleaning compositions, having a pH, as measured in a 10% solution in distilled water, from greater than 11 to about 14, comprising a soil swelling agent, thickening system and a divalent cation as defined by Claim 56.

Since, there is no motivation, suggestion or teaching in Feng, Culshaw et al, JP '597, or Ofosu-Asante, alone or in combination, of the desirability of practicing their inventions outside the disclosed pH range, there can be no expectation of success. It is therefore submitted that the cleaning compositions as defined by Claim 56 are non-obvious over and patentably distinguishable from Culshaw et al, Feng and JP '597 in combination with Ofosu-Asante and the rejection of Claim 56 under 35 U.S.C. § 103 has been overcome. Reconsideration is respectfully requested.

D. Claim 57 was rejected under 35 U.S.C. § 103(a) as being unpatentable over Culshaw et al in view of JP '597 or Feng in view of Culshaw et al and JP '597 as applied to previous claims, and further in view of WO 99/19441 (hereinafter referred to as "WO '441").

The Examiner relied on his earlier assertions regarding the disclosures of Culshaw et al and Feng, and asserted that WO '441 teaches a cleaning and disinfecting composition which provides effective cleaning, disinfecting and shine performance, where the composition comprises a surfactant system and antimicrobial compounds and/or a peroxygen bleach. Furthermore, the Examiner alleged that WO '441 further discloses a composition, which may be packaged in a spray dispenser, preferably a spray dispenser with a trigger.

However, as will be set forth in detail below, it is submitted that the hard surface cleaning product as defined by Claim 57 is non-obvious over and patentably distinguishable from Culshaw et al, Feng and JP '597 in view of WO '441. Accordingly, this rejection is traversed and reconsideration is respectfully requested.

WO '441 also discloses that pH values for the compositions taught in WO '441 are less than 9 (See examples in WO '441). WO'441 does not resolve the deficiencies of Culshaw et al, Feng and JP'597. Moreover, Culshaw et al, Feng and JP '597 in combination with WO '441 do not render the limitations of Claim 57 obvious. Applicants find no teaching or suggestion by these references relating to hard surface cleaning products having a composition with a soil swelling agent and thickening system, having a pH, as measured in a 10% solution in distilled water, from greater than 11 to about 14, and a spray dispenser as defined by Claim 57. Rather, Culshaw et al, Feng and JP '597 merely teach methods and compositions for cleaning, while WO '441 discloses a broad combination of surfactants for the surfactant system. The combination of these references fails to teach or suggest a cleaning composition as set forth in Claim 57, particularly where the composition provides a combination of good sprayability and cling, when

Application No. 09/909,288 Reply Date July 2, 2004

Reply to Official Action (Paper No. 12) of April 2, 2004

applied to soiled surfaces.

As noted above, the Examiner cannot pick and choose among individual elements of assorted parts of references to recreate the claimed invention, the Examiner has some burden to show some teaching or suggestion in references and to support their use in the particular claimed combinations. *Smith-Kline Diagnostics, Inc. v. Helena Laboratories, Corp.*, supra. As such, the combination of any of these references fails to teach or suggest a cleaning composition as set forth in Claim 57.

It is therefore submitted that the cleaning products as defined by Claim 57 are non-obvious over and patentably distinguishable from Culshaw et al, Feng and JP '597 in combination with WO '441 and the rejection of Claim 57 under 35 U.S.C. § 103 has been overcome. Reconsideration is respectfully requested.

# **CONCLUSION**

It is believed that the above remarks represent a complete response to the Examiner's rejections under 35 U.S.C. § 103, placing the present application in condition for allowance. Reconsideration and an early allowance are requested.

Respectfully submitted,

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**Abstract** 

(57)【要約】

【構成】

(A)動的光散乱法による平均粒径 10~5000nm、電気泳動光散乱法による & 電位の絶対値 30mV 以上及び粉末 X 線回折法による純度 90%以上の粘土鉱物 0.01~2.9 重量%と、(B)陰イオン性及び非イオン性界面活性剤の中から選ばれた少なくとも 1 種の界面活性剤 6.0~90 重量%とを含有する液体洗浄剤組成物である。

#### 【効果】

特定の性状を有する粘土鉱物を配合することで、使用するに際して好ましい粘度と容器取り出し時の糸引きなどがない良好な液性を備えた液体洗浄剤組成物が得られる。

# Claims

【特許請求の範囲】

#### 【請求項1】

(A)動的光散乱法による平均粒径 10~5000nm、電気泳動光散乱法によるぐ電位の絶対値 30mV 以上及び粉末 X 線回折法による純度90%以上の粘土鉱物 0.01~2.9 重量%と、(B)陰イオン性及び非イオン性界面活性剤の中から選ばれた少なくとも 1 種の界面活性剤 6.0~90 重量%とを含有することを特徴とする液体洗浄剤組成物。

# 【請求項2】

(A)成分の粘土鉱物が Li 型、Na 型又は K 型粘土鉱物である請求項 1 記載の液体洗浄剤組成物。

【請求項3】

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Agata discernment (1 other)

(57) [Abstract]

[Constitution]

It is a liquid detergent composition which contains detergent 6.0~90 weight% of at least 1 kind which with (A) dynamic light scattering method with average particle diameter 10~5000 nm, electrophoresis light scattering method with absolute value 30 mV or greater and powder x-ray diffraction of; zeelectric potential is chosen from clay mineral 0.01~2.9 weight% and (B) anionic of the purity 90 % or more and midst of nonionic surfactant.

[Effect(s)]

When you use by fact that clay mineral which possesses specific properties is combined, liquid detergent composition which has satisfactory liquid whichdoes not have desirable viscosity and thread pulling etc at time of the container removal is acquired.

[Claim(s)]

[Claim 1]

detergent 6.0~90 weight% of at least 1 kind which with (A) dynamic light scattering method with average particle diameter 10~5000 nm, electrophoresis light scattering method with the absolute value 30 mV or greater and powder x-ray diffraction of;ze electric potential is chosen from the clay mineral 0.01~2.9 weight% and (B) anionic of purity 90 % or more and midst of nonionic surfactant iscontained liquid detergent composition。 which densely is made feature

[Claim 2]

liquid detergent composition. which is stated in Claim 1 where clay mineral of (A) component is Li type. Na type or type K clay mineral

[Claim 3]

(A)成分の粘土鉱物が多価金属イオン置換粘土 鉱物である請求項 1 記載の液体洗浄剤組成 物。

# 【請求項4】

多価金属イオンがアルカリ土類金属イオンである請求項3記載の液体洗浄剤組成物。

# 【請求項5】

多価金属イオン置換粘土鉱物が、粘土鉱物中の交換性陽イオンの少なくとも 40 当量%が多価金属イオンで置換されたものである請求項 3 又は4記載の液体洗浄剤組成物。

# Specification

【発明の詳細な説明】

[0001]

#### 【産業上の利用分野】

本発明は、新規な液体洗浄剤組成物、さらに詳しくは、特定の粘土鉱物を配合して成る使用感に優れた液性を有する液体洗浄剤組成物に関するものである。

# [0002]

# 【従来の技術】

これまで、衣料洗浄用、台所洗浄用、窓ガラス洗浄用、浴室洗浄用、浴槽洗浄用、全身洗浄用、洗顔用、洗髪用、便器用、住居用などの洗浄剤に対し、好ましい液性を付与するために、粘度調整剤として、有機系、高分子系あるいは無機粘土鉱物などが用いられている。

ここで、好ましい液性とは、使いやすい粘度を有し、容器からの取り出し時に糸引きなどが生じない、すなわち、液切れが良いなどの性状をもつことを示す。

#### [0003]

しかしながら、これらの増粘剤の中で、有機系 増粘剤は増粘効果が小さいという欠点がある し、また高分子系増粘剤は、それを配合した液 体洗浄剤を容器から取り出す際に糸引きが生じ たり、該洗浄剤に電解質を添加した場合に著し く増粘効果が低下するなどの欠点を有してい る。

# [0004]

一方、粘土鉱物系の増粘剤は、高分子系増粘剤と同等の増粘効果を示すとともに、安価で、し

liquid detergent composition. which is stated in Claim 1 where clay mineral of (A) component is polyvalent metal ion exchange clay mineral

#### [Claim 4]

liquid detergent composition. which is stated in Claim 3 where polyvalent metal ion is the alkaline earth metal ion

#### [Claim 5]

polyvalent metal ion exchange clay mineral, liquid detergent composition, which is stated in Claim 3 or 4 which is somethingwhere at least 40 equivalent% of exchangeable cation in clay mineral are substituted with polyvalent metal ion

# [Description of the Invention]

[0001]

# [Field of Industrial Application]

As for this invention, novel liquid detergent composition, furthermore as for details, combining thespecific clay mineral, it is something regarding liquid detergent composition which possesses liquid which is superior in use feel which becomes.

# [0002]

# [Prior Art]

So far, in order to grant desirable liquid vis-a-vis for clothing cleaning, kitchen cleaning, window glass cleaning, bathroom cleaning, bath cleaning, whole body cleaning, face washing, for hair washing, for toilet and or other detergent for household, organic type, polymer systemor inorganic clay mineral etc is used as viscosity adjusting medicine.

Here, desirable liquid, it possesses viscosity which it is easy touse, thread pulling etc does not occur when removing from container, ithas or other properties where namely, liquid cut off is good it shows densely.

# [0003]

But, in these thickener, as for organic type thickener there is a deficiency that thickening effect is small, when and, in addition as for polymer thickener, thread pulling occurs occasion where liquid detergent which combines that is removedfrom container, adds electrolyte to said detergent it has possessed or other deficiency where thickening effect decreases considerably.

# [0004]

On one hand, thickener of clay mineral type as thickening effect which is equal to polymer thickener is shown, with

かもそれを配合した液体洗浄剤を容器から取り 出す際の液切れが良いなどの利点を有してい る。

# [0005]

粘土鉱物の増粘作用は、一般に、次のような機 構で生じるものと考えられている。

増粘剤として用いられる粘土鉱物は、層状の結晶が重なって粒子を形成しており、その層間には交換性をもつ種々の陽イオン、例えばナトリウムイオン、カルシウムイオン、鉄イオンなどがあり、粘土鉱物を水中に分散すると、この層間イオンが水和することにより、層間が拡大して粒子が膨張する。

その結果、粘土鉱物の粒子は薄片状に分離する。

この薄片の表面の電荷は負で、端面の電荷は正となる。

この電荷の違いにより、水中に分散した薄片は、たがいに表面と端部を接するような構造、いわゆる「カードハウス構造」を形成して粘土鉱物分散系を増粘する。

#### [0006]

しかしながら、洗浄剤組成物では、多くの場合、 電解質が共存することにより、薄片状粒子表面 の負電荷が中和され凝集を起こしやすくなり、 分散安定性が低下するとともに増粘効果が低 下する傾向がある。

さらに、より安価な天然産出の粘土鉱物を用いた場合には、増粘効果や分散安定性が産出地、あるいは同一産出地にあっても採取場所の違いにより変動したりするので、洗浄剤組成物への使用が限定されている。

#### [0007]

したがって、電解質共存下でも、少量の添加で 高い増粘効果を示し、しかも容器からの取り出 し時に糸引きなどが生じない液切れの良い、粘 土鉱物を配合した洗浄剤組成物を得ることは、 これまで困難であった。

# [8000]

他方、粘土鉱物の改質について、先に本発明 者らは、(1)膨潤力が 10ml/2g 以上の水膨潤性 三層粘土を含む懸濁液を 50000sec<sup>-1</sup> 以上の剪 断速度下で処理する方法(特開平 5-97500 号公 報)、(2)さらに剪断処理された懸濁液を 4000G inexpensive, furthermore case where liquid detergent which combines that is removed from container has had the or other benefit where liquid cut off is good.

# [0005]

thickening action of clay mineral generally, is thought thing which it occurs with next kind of mechanism.

When clay mineral which is used as thickener, crystal of layer being piled up, forms particle, is a various cation, for example sodium ion, potassium ion, magnesium ion, calcium ion, iron ion etc which has exchanging property in interlayer, disperses clay mineral to underwater, interlayer expanding this interlayer ion by hydration doing, particle does blistering.

As a result, it separates particle of clay mineral into flaky.

As for electric charge of surface of this thin piece with negative number, asfor electric charge of endface it becomes correct.

Due to difference of this electric charge, mutually surface and end forming structure, so-called "house-of-cards structure" which touches, clay mineral dispersion increased viscosity it does the thin piece which is dispersed to underwater.

#### [0006

But, as with detergent composition, in many cases, negative charge of flaky particle surface isneutralized due to fact that electrolyte coexists, and cohesion becomes easy to happen, dispersion stability decreases, there is a tendency where thickening effect decreases.

Furthermore, when from clay mineral of inexpensive natural product coming out is used, the thickening effect and dispersion stability production district, or being in same production district, because itfluctuates with difference of recovery site, use to detergent composition is limited.

# [0007]

Therefore, even under electrolyte coexisting, it was difficult so far toobtain detergent composition where it shows high thickening effect with addition of the trace, furthermore liquid cut off which thread pulling etc does not occur whenremoving from container is good, combines clay mineral.

# [8000]

Concerning improvement of other, clay mineral, first these inventors method which treats suspension to which (1) swelling power includes water-swellability three layers clay of 10 ml/2 g or more under shear rate of 50000 s<sup>-1</sup> or more (Japan Unexamined Patent Publication Hei 5-97500

以上の遠心加速度で遠心分離したのち、上澄み液を回収する方法(特開平 5-263359 号公報)、(3)平均粒径 100~5000nm、イオン交換性陽イオン量の少なくとも 70 当量%に相当する量のアルカリ金属イオン量及びスメクタイト 95 重量%を含む粘土鉱物含有水性懸濁液に、多価金属イオン含有水溶液を加えてイオン交換処理し、イオン交換性陽イオン量の少なくとも 70 当量%が多価金属イオンで置換されたスメクタイトを形成させたのち、これを分離回収し、所望により水洗する方法(特願平 5-142160 号、特願平5-333949号)を提案した。

しかしながら、これらの方法で改質された粘土鉱物は、いずれも繊維処理剤用に用いられるものであって、洗浄剤組成物に配合するものではなく、したがって、洗浄剤組成物中における前記改質方法で得られた粘土鉱物の増粘効果については知られていなかった。

# [0009]

# 【発明が解決しようとする課題】

本発明は、このような従来の粘土鉱物系増粘剤がもつ欠点を克服し、高い増粘効果を有し、分散安定性に優れた粘土鉱物を配合し、粘度のばらつきがなく、使用感に優れ、かつ容器からの取り出し時に液切れがよい液体洗浄剤組成物を提供することを目的としてなされたものである。

# [0010]

# 【課題を解決するための手段】

本発明者らは、前記の好ましい特性を有する液体洗浄剤組成物を開発すべく種々の検討を重ねた結果、特定の平均粒径、特定のぐ電位、特定の純度を有する粘土鉱物と、陰イオン性及び非イオン性界面活性剤の中から選ばれた少なくとも1種の界面活性剤とを、それぞれ所定の割合で含有する洗浄剤組成物が、その目的に適合しうることを見出し、この知見に基づいて本発明をなすに至った。

# [0011]

disclosure), (2) furthermore the shear suspension which was treated with centrifugation acceleration of 4000 G or greater the centrifugal separation after doing, supernatant method which recovers (Japan Unexamined Patent Publication Hei 5-263359 disclosure), In alkali metal ion quantity of quantity which is suitable at least to 70 equivalent% of (3) average particle diameter 100~5000 nm, ion exchange property positive ion amount and clay mineral content aqueous suspension liquid which includes smectite 95 weight%, including polyvalent metal ion -containing aqueous solution, the ion exchange treatment it does after forming smectite where at least 70 equivalent% of the ion exchange property positive ion amount are substituted with polyvalent metal ion, separation and recovery itdoes this, method (Japan Patent Application Hei 5-142160 number and Japan Patent Application Hei 5-333949 number) which water wash is done was proposed with desire.

But, as for clay mineral which is improved with these method, beingsomething which in each case is used for one for fiber treatment medicine, it is not something which it combines to detergent composition, therefore, concerning thickening effect of clay mineral which is acquired with theaforementioned improvement method in in detergent composition it was not known.

#### [0009]

# [Problems to be Solved by the Invention]

this invention overcomes deficiency which this kind of conventional clay mineral thickener has, possesses high thickening effect, combines clay mineral which is superior in the dispersion stability, is not a scatter of viscosity, is superior in use feel, it issomething which it is possible liquid detergent composition where at same time the liquid cut off is good when removing from container is offered densely as objective.

# [0010]

# [Means to Solve the Problems]

As for these inventors, in order that liquid detergent composition which possesses characteristic whose description above is desirable is developed as for result ofrepeating various examination, specific average particle diameter, specific;ze electricpotential, detergent composition which contains detergent of at least 1 kind which ischosen from midst of clay mineral and anionic and nonionic surfactant whichpossess specific purity, at respective predetermined ratio, It can conform to objective, you discovered densely, forming this invention you reached point of on basis of this knowledge.

[0011]

すなわち、本発明は、(A)動的光散乱法による 平均粒径 10~5000nm、電気泳動光散乱法によ るぐ電位の絶対値 30mV 以上及び粉末 X 線回 折法による純度 90%以上の粘土鉱物 0.01~2.9 重量%と、(B)陰イオン性及び非イオン性界面活 性剤の中から選ばれた少なくとも 1 種の界面活 性剤 6.0~90 重量%とを含有することを特徴とす る液体洗浄剤組成物を提供するものである。

# [0012]

本発明の液体洗浄剤組成物において、(A)成分として用いられる粘土鉱物の原料としては、例えばモンモリロナイト、バイデライト、ノントロナイト、サポナイト、ヘクトライト、ソーコナイト、スチブンサイトなどのスメクタイト及び膨潤性の雲母などがある。

これらの粘土鉱物は層間に水分子を伴った交換性のイオンを有しており、有機複合体を形成する、膨潤能を有するなど、他の粘土鉱物とは異なった性質を示す。

このようなスメクタイトには、天然産出品と合成品があり、天然産出のスメクタイトとしては、例えばモンモリロナイトを含有するものとして、クニミネ工業(株)社から、クニピアG及びクニピアF、アメリカンコロイド社からウエスタンボンド、ドレッサーミネラルズ社からのイエローストーンなどが、サポナイトを含有するものとして、バンダービルド社からビーガム K などが、また、ヘクトライトを含有するものとして、アメリカンコロイド社からヘクタブライト AW、ヘクタブライト 200 及びベントン EW、ナショナルリード社からマカロイドなどが市販されている。

また、合成スメクタイトとしては、例えば水澤化学工業(株)社からイオナイト H、コープケミカル(株)社から SWN、SAN、ラポルテインダストリー社からラポナイトなどが市販されている。

# [0013]

膨潤性の雲母としては、コープケミカル(株)社製の膨潤性合成雲母 ME シリーズ、トピー工業(株)社製のナトリウム四ケイ素雲母(商品名、DP-DM 及び DM クリーン)などが挙げられる。

# [0014]

また、(A)成分の粘土鉱物の原料として、酸性白 土のアルカリ処理物も用いることができる。 namely, this invention contains detergent 6.0~90 weight% of at least 1 kind which with (A) dynamic light scattering method with average particle diameter 10~5000 nm, electrophoresis light scattering method with absolute value 30 mV or greater and powder x-ray diffraction of;ze electric potentialis chosen from clay mineral 0.01~2.9 weight% and (B) anionic of purity 90% or more and midstof nonionic surfactant is something which offers liquid detergent composition which densely is madefeature.

# [0012]

for example montmorillonite (DANA 71.3.1a.2), beidellite, nontronite, saponite (DANA 71.3.1b.2), hectorite (DANA 71.3.1b.4), there is a sauconite, stevensite or other smectite and a mica etc of swellable as starting material of clay mineral which is used in liquid detergent composition of this invention, as (A) component.

These clay mineral have had ion of exchanging property which accompanies the water molecule interlayer, form organic composite, such as possesses swelling ability, theother clay mineral property which differs is shown.

As, is natural product exhibition and synthetic product in this kind of smectite, contains for example montmorillonite (DANA 71.3.1a.2) as smectite of natural product coming out, from Kinimine Industries Co., Ltd. corporation, Kunipia G and from Kunipia F. American colloid corporation yellow stone etcfrom Western bond, dresser mineral  $\mathbb{Z}$  corporation, as contains saponite (DANA 71.3.1b.2), from the Vanda coerulea Griff. ex Lindl.—build corporation V-gum T, V-gum HV, V-gum F and V-gum K etc, in addition, From to American colloid corporation to  $\mathcal{D}$  tab light/write AW, the macaloid etc is marketed from  $\mathcal{D}$  tab light/write 200 and bentonite EW, national lead corporation as contains hectorite (DANA 71.3.1b.4).

In addition, from for example Mizusawa Industrial Chemicals Ltd. (DB 69-066-9049) corporation from IONA I jp7 H, Co-Op Chemical Co. Ltd. (DB 69-059-9402) corporation Laponite etc is marketed from SWN, SAN, Laporte industry corporation as synthetic smectite.

# [0013]

As mica of swellable, you can list sodium tetrasilicic mica (tradename, DP-DM and DM clean) etc of swellable synthetic mica MEseries, Topy Industries Ltd. (DB 69-054-4341) Ltd. supplied of Co-Op Chemical Co. Ltd. (DB 69-059-9402) supplied.

# [0014]

In addition, you can use also alkali treatment ones of acidic clay as starting material of clay mineral of (A) component.

この酸性白土は、通常 1 重量%水溶液分散液の pH が  $5\sim6$  以下、膨潤度が 10ml/2g 以下、 $SiO_2$  と  $Al_2O_3$  の 含 有 量 が モ ル 比 で  $SiO_2/Al_2O_3=6\sim10$  のものである。

このようなものとしては、例えば中条、小戸、上 赤谷、糸魚川、水澤、川崎、松根、三川、青梅、 上砂見産の酸性白土や、これらの酸性白土と 類似の性質を示す英国産のフラーズ・アース (Fuller's earth)、米国産のフロライド・アース (Floride earth)、ドイツ産のワルケル・エルデ (Warkel erde)などが挙げられる。

酸性白土中に存在する交換性の陽イオンとしてはナトリウムイオン、カリウムイオン、マグネシウムイオン、鉄イオンなどがある。

これらの酸性白土はアルカリ処理することにより、上記の粘土鉱物と同様に扱うことができる。

#### [0015]

これらの粘土鉱物を本発明組成物の(A)成分として用いるには、動的光散乱法により測定した平均粒径が 10~5000nm、電気泳動光散乱法により測定したく電位の絶対値が 30mV 以上、粉末 X 線回折法により求めた純度が 90%以上であることが必要である。

#### [0016]

この平均粒径及びく電位は、試料を約 60ppmの濃度で蒸留水に加えて 60 分間超音波分散させたものについて、平均粒径は温度 20 deg C、屈折率 1.331、粘度 0.951cP、角度 90 度の条件下で光散乱法により粘土鉱物の膨潤性ゲル粒子の粒径を測定したもの、く電位は電気泳動光散乱光度計を用い、散乱角 20 度、室温で測定したものを示す。

また、純度は粉末法により X 線回折を行い、得られた X 線回折図において、粘土鉱物に帰属するピーク面積の総和 Sc とその他の結晶に帰属するピーク面積の総和 Sx とを求め、式

粘土鉱物の純度(%)=Sc/(Sc+Sx)×100 によって求めた値である。

# [0017]

この粘土鉱物の平均粒径が 10nm 未満では洗 浄剤組成物を増粘するのに多量の粘土鉱物が This acidic clay, usually pH of 1 weight% aqueous solution dispersion 5 - 6 or fewer, degree of swelling 10 ml/2 g or less,  $SiO_2$  and the content of  $Al_2O_3$  being mole ratio, is something of  $SiO_2/Al_2O_3=6\sim10$ .

As this kind of ones, for example Chujo, small door, upper Akatani, the yarn fish river, Mizusawa, Kawasaki, pine root, Mikawa, acidic clay and these acidic clay of Sunami product on Ome, and Fuller's earth of England domestic manufacture which showssimilar property (Fuller's earth), fluoride \* ground of American (Floride earth), 7 jpl1 of the Germany product you can list jpl1 \* L.  $\vec{\tau}$  (Warkel erde) etc.

There is a sodium ion, potassium ion, magnesium ion, iron ion etc as cation of exchanging property which exists in the acidic clay.

It handles these acidic clay in same way as above-mentioned clay mineral by alkali treatment doing, it is possible densely.

# [0015]

To use these clay mineral, as (A) component of this invention composition average particle diameter which wasmeasured due to dynamic light scattering method absolute value of the;ze electric potential whichwas measured due to 10 - 5000 nm, electrophoresis light scattering method purity which was sought with 30 mV or greater, powder x-ray diffraction is 90% or more, it is necessary densely.

# [0016]

As for this average particle diameter and;ze electric potential, concerning those which sample with concentration of approximately 60 ppm in addition to the distilled water 60 min ultrasonic dispersing do, as for average particle diameter under condition of temperature 20 deg C, index of refraction 1.3 31, viscosity 0.951 cP, angle 90 degrees thosewhich measured particle diameter of swellable gel particle of clay mineral due to light scattering method.; ze electric potential shows those which were measured with scattering angle 20-degree, room temperature making use of electrophoresis light scattering photometer.

In addition, purity does X-ray diffraction with powder method, in clay mineral seeks sum Sx of peak area which assignment is done from sum Sc and other crystal of peak area which assignment is done in x-ray diffraction pattern which is acquired, system

purity of clay mineral (%) =Sc/(Sc+Sx) X 100

So it is a value which was sought.

# [0017]

average particle diameter of this clay mineral under 10 nm clay mineral of large amount beingnecessary in order

必要であり、また 5000nm を超えると安定した分散状態が得られない上、洗浄剤組成物の使用時に被洗浄面を傷付けたりする。

増粘効果、分散安定性及び被洗浄面に対する 傷付け防止性などの面から、好ましい平均粒径 は 200~2000nm の範囲である。

#### [0018]

また、
く電位の絶対値が 30mV 未満では粘土 粒子が凝縮しやすくなり、洗浄剤組成物におい て、凝集物の沈降が生じたりして分散安定性が 低下する。

さらに、粘土鉱物、特に天然から採取したものには、カルサイト、トリジマイト、クリストバライト、石英、各種無機物などの非膨潤性のきょう雑物が含まれており、これらは洗浄剤組成物中で、沈降したり、溶解して電解質を放出したりして、商品の外観や粘土鉱物の分散性を損なう原因となる。

したがって、粘土鉱物の純度は 90%以上である ことが必要であり、特に 95%以上が好ましい。

# [0019]

本発明において、(A)成分として用いられる前記性状を有する粘土鉱物は、例えば単に原料粘土鉱物を水中に懸濁し、その上澄み液を分離することによっても得ることができるが、原料の粘土鉱物を水中に懸濁し、これを 50000sec<sup>-1</sup>以上の剪断速度でかき混ぜながら膨潤させたのち、その上澄み液を分離することによって調製するのが有利である。

#### [0020]

この膨潤処理は、原料粘土鉱物を水で膨潤させるとともに増粘効果の優れた成分を上澄み液として、前記のきょう雑物、例えば、カルサイト、トリジマイト、クリストバライト、石英などから分離するための処理であり、したがって、湿式法で行うことが必要であって、空気分級などの乾式法を用いることはできない。

# [0021]

前記したように、懸濁処理におけるかき混ぜは、50000sec<sup>-1</sup>以上、好ましくは 70000sec<sup>-1</sup>以上 の超高速剪断速度下で行うのが有利であるが、この際の所要時間は、剪断速度が高ければ短くなり、剪断速度が低ければ長くなるが、通常 1

increased viscosity to do detergent composition, in addition when itexceeds 5000 nm, in addition to fact that dispersed form which isstabilized is not acquired, surface being washed is damaged when using detergent composition.

From damaging prevention property or other aspect for thickening effect. dispersion stability and surface being washed, the desirable average particle diameter is range of 200 - 2000 nm.

# [0018]

In addition, absolute value of;ze electric potential under 30 mV the clay particle condensation becomes easy to do, settling of agglomerate occurringin detergent composition, dispersion stability decreases.

Furthermore, calcite, tridymite (DANA 75.1.2.1), cristobalite (DANA 75.1.1.1), foreign matter of quartz, various inorganic substance or other unswellable to be included by any which recover from clay mineral, especially natural, these doing, in detergent composition, settling melting, discharging electrolyte, it becomes external appearance of product and cause which impairs dispersibility of clay mineral.

Therefore, purity of clay mineral is 90% or more, being necessarydensely, especially 95% or more is desirable.

#### [0019]

Regarding to this invention, for example starting material clay mineral suspension it does the clay mineral which possesses aforementioned properties which is used as (A) component, simply in underwater, it separates supernatant with densely it can acquire, but while suspension doing clay mineral of starting material inunderwater, stirring this with shear rate of 50000 s<sup>-1</sup> or more the swelling after doing, It is profitable to manufacture supernatant is separated with densely.

# [0020]

This swelling treatment, as starting material clay mineral swelling it does with water, with the component where thickening effect is superior as supernatant, aforementioned foreign matter. for example calcite. tridymite (DANA 75.1.2.1), cristobalite (DANA 75.1.1.1), in treatment in order to separate from the quartz etc, therefore, it does with wet method, being necessary densely, it is not possible to use air part class or other dry method.

# [0021]

As before inscribed, as for stirring in suspension treating, it isprofitable to do under ultra-high speed shear rate of 50000 s<sup>-1</sup> or more and above the preferably 70000 s<sup>-1</sup>, but in this case if as for time required, shear rate is high, if itbecomes short and shear rate is low, it becomes long, but usually it is l

秒ないし 24 時間、好ましくは 1 分~5 時間である。

これが短すぎると十分な剪断が行われないば かりか、上澄み液中の粘土鉱物の含有量が減 り経済的でなく、またあまり長すぎると粘土鉱物 の非晶質化を生じ増粘効果を低下させる。

# [0022]

この際の剪断手段としては、狭い間隙を通して、剪断、破壊、分散作用を与えるホモジナイザー、コロイドミル、ジェット粉砕器などが好適である。

また、この際の間隙の幅は 0.5mm 以下にする のが望ましい。

# [0023]

また、この際に効果的な剪断を得るためには、 粘土鉱物の懸濁液の、B型粘度計による25 deg Cでの粘度を50000cP以下、好ましくは1000cP 以下にすることが望ましい。

この粘度が 50000cP を超えると、ずり応力が著しく上昇するため、50000sec<sup>-1</sup>以上の剪断速度を得ることができにくくなるし、場合によっては懸濁液の降伏値を超え、かき混ぜ部分に空回りを生じ、懸濁液に十分な剪断力を加えられなくなる。

# [0024]

次に、上澄み液の分離は遠心分離により行うのが有利である。

この場合、目的とする粘土鉱物を得るためには、通常 4000G 以上、好ましくは 6000G 以上の加速度で遠心分離したのち、上澄み液を回収する。

この加速度が 4000G 未満では増粘効果が低い 大きな粘土粒子や、微細な不純物あるいは非 晶質の粘土成分などが十分に除去できず、優 れた増粘効果をもち、分散安定性に優れた粘土 鉱物が得られにくい。

この遠心分離による処理時間は 5 秒ないし 100 時間程度、好ましくは 1 分ないし 24 時間である。

このかきまぜ処理や上澄み液を取得する処理は、温度  $0\sim105\deg C$  の範囲で行うことができるが、 $20\sim90\deg C$  の範囲で行うのが好ましい。

#### [0025]

second or 24 hours, preferably 1 min~5 hours.

When this is too short, when sufficient shear not only not being done, the content of clay mineral in supernatant decreases and not to be a economical, inaddition is too long excessively, it causes amorphous transformation of clay mineral and thickening effect decreases.

# [0022]

In this case shear, destruction and homogenizer, colloid mill, jet grinder etc which gives dispersing action are ideal through narrow gap as shear means.

In addition, in this case as for width of gap it is desirable to make 0.5 mm or less.

# [0023]

In addition, in order to obtain effective shear in this case, with B type viscometer of suspension of clay mineral viscosity with 25 deg C is designated as 50000 cP or less, preferably 1000 cP or less, it is desirable densely.

When this viscosity exceeds 50000 cP, because shear stress risesconsiderably, it becomes difficult be able to acquire shear rate of 50000 s<sup>-1</sup> or more and, when depending to exceed yield point of the suspension, to cause empty rotation in stirring portion, it stops being added sufficient shear stress to suspension.

# [0024]

Next, as for separation of supernatant it is profitable to do with the centrifugal separation .

In this case, in order to obtain clay mineral which is made objective, centrifugal separation after doing, supernatant it recovers with acceleration of usually 4000 G or greater, preferably 6000 G or greater.

Large not be able to remove clay particle and microscopic impurity or clay component etc of amorphous where this acceleration under 4000 G thickening effect is low in the fully, clay mineral which is superior in dispersion stability with thickening effect whichis superior, is difficult to be acquired.

process time 5 second or 100 hour extent, preferably 1 min or is 24 hours with this centrifugal separation.

It does this stirring treatment and treatment which acquires the supernatant, in range of temperature  $0\sim105~\text{deg C}$ , it is possible densely, but it is desirable to do in range of 20 - 90 deg C.

# [0025]

このようにして得た上澄み液中の粘土鉱物は、通常、Li型、Na型、K型などのアルカリ金属イオン型で、動的光散乱法により測定した平均粒径が  $10\sim5000$ nm、電気泳動光散乱法によって測定した $\xi$ 電位の絶対値が 30mV 以上、及び粉末 X線回折法によって測定した純度が 90%以上である。

この上澄み液をそのまま洗浄剤組成物に配合してもよいし、また、場合によっては、濃縮、あるいは、乾燥して粉体状、フレーク状にして洗浄剤組成物に配合してもよい。

#### [0026]

さらに、本発明においては、場合により、この粘 土鉱物のイオン交換反応を行い、多価金属イオ ン置換粘土鉱物としても用いることができる。

このものは、洗浄剤組成物中での増粘効果を 一層高めるのに適している。

また、この一層高い増粘効果を得るためには、 多価金属イオンの置換率が 40 当量%以上であ ることが望ましい。

#### [0027]

この際に用いられる多価金属イオンとしてはカルシウムイオン、マグネシウムイオン、バリウムイオン、ストロンチウムイオンなどのアルカリ土類金属イオンや、亜鉛イオン、ジルコニウムイオン、チタニウムイオン、アルミニウムイオンなどがあるが、特に好ましいのはアルカリ土類金属イオンである。

# [0028]

このイオン交換は、前記の上澄み液に該多価 金属イオンを含む水溶液を添加して行うのが有 利である。

多価金属イオンを含む水溶液は、対応する多価 金属の水溶性塩を、水に溶解することによって 調製される。

この水溶液は多価金属イオンを飽和濃度まで含むものであればよいが、あまり高濃度になると、陽イオンの交換が不均一になるので、通常は20重量%以下のものを用いるのが好ましい。

イオン交換後、生成した多価金属イオン置換粘 土鉱物はゲル状となるが、沈降分離、遠心分離 などにより回収し、必要に応じて水洗して過剰 の多価金属イオンを除去する。

このゲルをそのまま洗浄剤組成物に配合しても

As for clay mineral in supernatant which it acquires in this way, absolute value of the;ze electric potential which average particle diameter which usually, with the Li type. Na type, type K or other alkali metal ion type, was measured due to dynamic light scattering method measured with 10 - 5000 nm, electrophoresis light scattering method 30 mV or greater, and purity which was measured with powder x-ray diffraction is 90%or more.

It is possible to combine this supernatant to detergent composition that way and, inaddition, when depending, concentration, or, drying, it is possible tocombine to detergent composition powder body condition, to flake.

#### [0026]

Furthermore, regarding to this invention, from when, it does ion exchange reaction of this clay mineral, as polyvalent metal ion exchange clay mineral it can use.

This is suitable, although thickening effect in detergent composition is raised more.

In addition, in order this furthermore to obtain high thickening effect, the substitution ratio of polyvalent metal ion is 40 equivalent % or more, it is desirable densely.

# [0027]

There is a calcium ion, magnesium ion, barium ion, strontium ion or other alkaline earth metal ion and a zinc ion, zirconium ion, titanium ion, aluminum ion etc, as polyvalent metal ion which is used in this case, but those where especially it is desirable are alkaline earth metal ion.

# [0028]

As for this ion exchange, adding aqueous solution which includes said polyvalent metal ion inaforementioned supernatant, it is profitable to do.

aqueous solution which includes polyvalent metal ion is manufactured water soluble salt of polyvalent metal which corresponds, is melted in water by densely.

This aqueous solution if something which includes polyvalent metal ion to saturation concentration itshould have been, but when excessively it becomes high concentration, becauseexchange of cation becomes nonuniform, usually it is desirable touse those of 20 weight % or less.

After ion exchange, polyvalent metal ion exchange clay mineral which is formed becomes gel, but itrecovers with sedimentation, centrifugal separation, etc according to need water wash does and removes polyvalent metal ion of excess.

It is possible to combine this gel to detergent composition that

よいし、また、場合によっては、濃縮、あるいは、 乾燥して粉体状、フレーク状にして洗浄剤組成 物に配合してもよい。

# [0029]

本発明の洗浄剤組成物においては、(A)成分として、前記の性状を有する粘土鉱物を 0.01~2.9 重量%の範囲で含有することが必要である。

この含有量が 0.01 重量%未満では増粘効果が 十分に発揮されないし、2.9 重量%を超えると凝 集粒子の沈降が生じるなど分散安定性が低下 する。

増粘効果及び分散安定性の面から、該粘土鉱物の好ましい含有量は 0.1~1.0 重量%の範囲である。

#### [0030]

次に、本発明の洗浄剤組成物においては、(B) 成分として、陰イオン性界面活性剤及び非イオン性界面活性剤の中から選ばれた少なくとも 1 種が用いられる。

該陰イオン性界面活性剤としては、通常の石ケン、スルホネート系、サルフェート系、ホスフェート系などのものが使用される。

ここで、石ケンとしては、例えば飽和あるいは不飽和( $C_6$ ~ $C_{30}$ )脂肪酸塩が挙げられる。

スルホネート系陰イオン性界面活性剤としては、例えば直鎖又は分枝鎖アルキル $(C_8\sim C_{23})$ ベンゼンスルホン酸塩、長鎖アルキル $(C_8\sim C_{22})$ スルホン酸塩、長鎖オレフィン $(C_8\sim C_{22})$ スルホン酸塩などが挙げられる。

またサルフェート系陰イオン性界面活性剤としては、例えば長鎖モノアルキル( $C_8\sim C_{22}$ )硫酸エステル塩、ポリオキシエチレン( $1\sim 6$  モル)長鎖エステル( $C_8\sim C_{22}$ )エーテル硫酸エステル塩、ポリオキシエチレン( $1\sim 6$  モル)アルキル( $C_8\sim C_{18}$ )フェニルエーテル硫酸エステル塩などが挙げられ、また、ホスフェート系陰イオン界面活性剤としては、例えば、長鎖モノアルキル、ジアルキル又はセスキ(各アルキル基の炭素数は  $8\sim 22$  である)リン酸塩、ポリオキシエチレン( $1\sim 6$  モル)モノアルキル、ジアルキル又はセスキアルキル(各アルキル基の炭素数は  $8\sim 22$  である)リン酸塩などが挙げられる。

これらの陰イオン性界面活性剤の対イオンとしての陽イオンは、例えばナトリウム、カリウム、マグネシウムなどのアルカリ金属又はアルカリ土類金属のイオン、モノエタノールアミン、ジェタ

way and, inaddition, when depending, concentration, or, drying, it is possible tocombine to detergent composition powder body condition, to flake.

#### [0029]

Regarding detergent composition of this invention, clay mineral which possesses theaforementioned properties as (A) component, is contained is necessarydensely in range of 0.01 - 2.9 weight%.

When this content under 0.01 weight% thickening effect is not shown and, exceeds 2.9 weight% in fully, settling of aggregated particle decreases such asoccurs dispersion stability.

From aspect of thickening effect and dispersion stability, content where said clay mineral is desirable is range of 0.1 - 1.0 weight%.

#### [0030]

Next, regarding detergent composition of this invention, it can use at least 1 kind which is chosen from midst of anionic surfactant and nonionic surfactant as (B) component.

As said anionic surfactant, conventional soap, sulfonate type, sulfate system, phosphate or other ones are used.

Here, you can list for example saturated or unsaturated  $(C_6 \sim C_{30})$  aliphatic acid salt as soap.

As sulfonate type anionic surfactant, you can list for example straight or branched alkyl ( $C_8 \sim C_{23}$ ) benzenesulfonate, long chain alkyl ( $C_8 \sim C_{22}$ ) sulfonate, long chain olefin ( $C_8 \sim C_{22}$ ) sulfonate etc.

In addition you can list for example long chain monoalkyl  $(C_8 \sim C_{22})$  sulfuric acid ester salt, polyoxyethylene (1 - 6 mole) long chain ester  $(C_8 \sim C_{22})$  ether sulfuric acid ester salt, polyoxyethylene (1 - 6 mole) alkyl  $(C_8 \sim C_{18})$  phenyl ether sulfuric acid ester salt etc as sulfate anionic surfactant, in addition, you can list for example long chain monoalkyl, dialkyl or sesqui (carbon number of each alkyl group is 8 - 22.) phosphate, polyoxyethylene (1 - 6 mole) monoalkyl, dialkyl or sesqui alkyl (carbon number of each alkyl group is 8 - 22.) phosphate etc as phosphate type anionic surfactant.

cation as counterion of these anionic surfactant is ion, monoethanolamine, diethanolamine, triethanolamine or other alkanolamine ion etc of for example sodium, potassium, magnesium or other alkali metal or alkaline earth

# JP1996151597A

ノールアミン、トリエタノールアミンなどのアルカ ノールアミンイオンなどである。

#### [0031]

一方、非イオン界面活性剤としては、例えばポリオキシエチレン( $1\sim20~$  モル)長鎖アルキル(第一級又は第二級  $C_8\sim C_{22}$ )エーテル、ポリオキシエチレン( $1\sim20~$  モル)アルキル( $C_8\sim C_{18}$ )フェニルエーテル、ポリオキシエチレンポリオキシプロピレンブロックコポリマーなどのオキシアルキレン付加化合物、高級脂肪酸アルカノールアミド又はそのアルキレンオキシド( $C_{12}\sim C_{14}$ )などが挙げられる。

# [0032]

本発明においては、これらの界面活性剤はそれぞれ単独で用いてもよいし、2 種以上組み合わせて用いてもよく、その配合量は 6.0~90 重量%の範囲で選ばれる。

# [0033]

また、本発明の液体洗浄剤組成物には、前記の必須成分に加えて、必要に応じ本発明の効果を損なわない範囲内で、例えば、グリセリン、ポリエチレングリコールなどの多価アルコール、キシレンスルホン酸塩、トルエンスルホン酸塩などのアリールスルホン酸塩やエタノールなどの可溶化剤、香料、色素、酵素、粘結剤、キレート剤、薬効成分、水溶性高分子などを添加することができる。

#### [0034]

# 【発明の効果】

本発明の液体洗浄剤組成物は、特定な性状を 有する粘土鉱物を含有する洗浄剤組成物であ り、その使用に供するに際して好ましい粘度と 容器取り出し時の糸引きなどがない良好な液性 を備えており、商品価値の高いものである。

# [0035]

#### 【実施例】

次に実施例により本発明をさらに詳しく説明する。

なお、例中の物性の測定と評価は以下の方法で行った。

# [0036]

(1)動的光散乱法による平均粒径

metal.

# [0031]

On one hand, you can list for example polyoxyethylene (1 - 20 mole) long chain alkyl (primary or secondary  $C_8 \sim C_{22}$ ) ether, polyoxyethylene (1 - 20 mole) alkyl ( $C_8 \sim C_{18}$ ) phenyl ether, polyoxyethylene polyoxypropylene block copolymer or other oxyalkylene adduct, higher aliphatic acid alkanol amide or alkylene oxide adduct, long chain type tertiary amine oxide ( $C_{12} \sim C_{14}$ ) etc as nonionic surfactant.

# [0032]

Regarding to this invention, it is possible to use these detergent respectively with alone and, 2 kinds or more combining, it is possible to use, the blended amount is chosen in range of 6.0 - 90 weight%, preferably 6.0~50 weight%.

# [0033]

In addition, to liquid detergent composition of this invention, inside range which doesnot impair effect of this invention in addition to aforementioned essential ingredient, according to need, for example glycerine, polyethylene glycol or other polyhydric alcohol, xylene sulfonate, toluene sulfonate or other aryl sulfonate and ethanol or other solubilizer, perfume and the dye, enzyme, thickener, chelator, active ingredient, water soluble polymer etc can be added.

# [0034]

# [Effects of the Invention]

liquid detergent composition of this invention when with detergent composition which contains clay mineral which possesses specific properties, it offers to use has thesatisfactory liquid which does not have desirable viscosity and thread pulling etc at time of container removal, it is something where commercial value is high.

# [0035]

#### [Working Example(s)]

Next this invention furthermore is explained in detail with Working Example .

Furthermore, it measured property in example and it appraised with method below.

# [0036]

With (1) dynamic light scattering method average particle diameter

純水中に粘土鉱物を分散し 60ppm の濃度としたものについて、動的光散乱光度計 DLS-800型(商品名、大塚電子工業社製)を用い、温度 20 deg C、屈折率 1.331、粘度 0.951cP、角度 90 度の条件で粒径測定を行った。

# [0037]

(2)電気泳動光散乱法による ζ 電位

純水中に粘土鉱物を分散し 60ppm の濃度としたものについて、電気泳動光散乱光度計 DLS-800 型(商品名、大塚電子工業社製)を用い、散乱角 20 度、温度 20 deg C で く電位を求めた。

# [0038]

# (3)純度

粘土鉱物の純度は粉末法により X 線回折を行い、得られた X 線回折図において、粘土鉱物に帰属するピーク面積の総和 Sc とその他の結晶に帰属するピーク面積の総和 Sx とを求め、式

粘土鉱物の純度(%)=Sc/(Sc+Sx)×100

によって求めた。

なお、X 線回折の測定に際しては、定量の標準的な測定条件を用い、最も強いピークがほぼ100%となるフルスケールで行った。

#### [0039]

(4)粘度の測定

B 型粘度計を用いて測定した。

# [0040]

(5)增粘効果

洗浄剤組成物の粘度と、その組成物より粘土鉱物を除いたものの粘度を測定し、前者より後者を差し引いたものを増粘効果とする。

#### [0041]

(6)粘土鉱物の洗浄剤組成物中での分散安定 性

所定の組成で配合した洗浄剤組成物について、配合後、100 日目に目視で判断して、濁り、離水、沈殿物などが生じたり、粘度の変化があっ

clay mineral was dispersed in pure water and grain size measurement was done with the condition of temperature 20 deg C, index of refraction 1.3 31, viscosity 0.951 cP, angle 90 degrees concerning those which are made concentration of 60 ppm, making use of dynamic light scattering photometer DLS-800 type (tradename, Otsuka Denshi K.K. (DB 70-451-5253) industrial supplied).

#### [0037]

With (2) electrophoresis light scattering method; ze electric potential

clay mineral was dispersed in pure water and; ze electric potential wassought with scattering angle 20-degree, temperature 20 deg C concerning those which are made concentration of 60 ppm, making use of electrophoresis light scattering photometer DLS-800 type (tradename, Otsuka Denshi K.K. (DB 70-451-5253) industrial supplied).

# [0038]

# (3) purity

purity of clay mineral does X-ray diffraction with powder method, in clay mineral seeks sum Sx of peak area which assignment is done from sum Sc and other crystal of peak area which assignment is done in x-ray diffraction pattern which is acquired, system

purity of clay mineral (%) =Sc/(Sc+Sx) X 100

So it sought.

Furthermore, it did with full scale where strongest peak almostbecomes 100% making use of standard measurement condition of quantification at time of themeasurement of X-ray diffraction.

#### [0039]

Measurement of (4) viscosity

It measured making use of B type viscometer.

# [0040]

# (5) thickening effect

viscosity of detergent composition and viscosity of those which exclude clay mineral from composition are measured, those which deduct the latter are designated as thickening effect from former.

# [0041]

dispersion stability in detergent composition of (6) clay mineral

After combining, in 100 th day judging with visual concerning the detergent composition which is combined with predetermined composition, those which those which the

たものを×、外観上、変化がなく、しかも粘度変化がなかったものをOとした。

#### [0042]

#### 実施例1

粘土鉱物の原料として山形県産のモンモリナイト(灼熱残分85重量%)を用い、この3.0kgを、純水50kgに加え、6日間かけて十分に膨潤させたのち、デカンテーションにより上層を全体の1/3容量回収する、いわゆる水たけ簸により精製を行った。

# [0043]

得られた粘土鉱物を含む懸濁液を乾燥し、粘土鉱物の純度を X 線回折法で測定したところ、98 重量%以上であった。

また粘土鉱物の組成分析を行った結果、イオン 交換性陽イオンの 95 重量%が Na イオンであっ た。

#### [0044]

次いで、この懸濁液を日立工機(株)製日立高速 冷却遠心機 SCR20B 型(ローター:RPR9-2 型。 回転半径:170mm)を用いて、回転数 8000rpm で 15 分間遠心分離を行い、上澄み液を回収した。

この上澄み液、すなわち、粘土分散液に含まれる粘土鉱物の純度、 と電位、 粒径を表 1 に示す。

# [0045]

この粘土鉱物分散液を粘土鉱物濃度が 15 重量%となるまで加熱濃縮した。

これとは別に AOS-Na(炭素数 14)2.9 重量%、 LES-Na(炭素数 13、エチレンオキシド平均付加 モル数 3)29.3 重量%、アミンオキシド 4.4 重量% を含む界面活性剤水溶液 1400 重量部を調製 し、これに上記の粘土鉱物分散濃縮液 100 重量 部を撹拌しながら徐々に加えた。

得られた洗浄剤組成物の組成、増粘効果及び 分散安定性を表 1 に示す。

#### [0046]

# 実施例2

5 リットルの純水に、塩化カルシウム二水和物 (純度 100%)を溶解し、CaO 換算 500ppm の水溶 turbidity, water release, precipitate etc occurs, has viscosity change on X, external appearance, is not change, furthermore do not have viscosity change were designated as 0.

# [0042]

# Working Example 1

Making use of montmorillonite (Ignition remnant 85 weight%) of produced in Yamagata Prefecture, these 3.0 kg, in additionto pure water 50 kg as starting material of clay mineral, 6 day applying, top layer 1/3 volume of entirety it recovers swelling after doing, with the decantation in fully, it refined with so-called water fungus 簸.

#### [0043]

suspension which includes clay mineral which it acquires was dried, when purity of clay mineral was measured with x-ray diffraction, they were 98 weight % or more.

In addition as for result of doing constituent analysis of clay mineral, 95 weight% of ion exchange property cation were Naion.

# [0044]

Next, it did 15 min centrifugal separation with rotation rate 8000 rpm this suspension making use of the Hitachi Koki Co. Ltd. (DB 69-053-6644) Ltd. make Hitachi high speed refrigerated centrifuge SCR20 B type (rotor:RPR9-type 2° radius:170 mm), supernatant recovered.

purity, ;ze electric potential of clay mineral which is included in this supernatant, namely, clay dispersion, particle diameter is shown in Table 1.

# [0045]

Until clay mineral concentration becomes 15 weight%, it heated concentrated this clay mineral dispersion.

While separately from this AOS-Na (carbon number 14) 2.9 weight%, LES-Na (carbon number 13, ethylene oxide average number of moles added 3) manufacturing the detergent aqueous solution 1400 parts by weight which includes 29.3 wt%, amine oxide 4.4 weight%, agitating above-mentioned clay mineral dispersed concentrated liquid 100 parts by weight in this it added gradually.

composition, thickening effect and dispersion stability of detergent composition which it acquires are shown in Table 1.

#### [0046]

# Working Example 2

calcium chloride dihydrate (purity 100%) was melted in pure water of 5 liter, aqueous solution of the CaO conversion 500

# 液を調製した。

この水溶液に、実施例1の粘土鉱物を含む上澄 み液(粘土鉱物1.0 重量%)150g を加え、7 時間 かき混ぜたのち、約15 時間静置した。

静置後、ビーカーの底部に形成された粘土鉱物 のゲル層を遠心分離(350rpm、10分)して回収し た。

# [0047]

得られたゲル中の粘土鉱物について組成分析 を行った結果、粘土鉱物のイオン交換性陽イオ ンの 88 当量%が Ca イオンに置換されていた。

この粘土鉱物の乾燥物における純度、 ぐ電位及び粒径を表 1 に示す。

また、この粘土鉱物を実施例 1 と同様な方法で配合して調製した洗浄剤組成物の組成、増粘効果及び分散安定性を表1に示す。

# [0048]

# 実施例3

粘土鉱物としてバンダービルト社製サポナイト (商品名:ビーカム T、灼熱残分 85.3 重量%)118g を、純水 4882g にかき混ぜながら加え、さらにホモジナイザー(キネマテカ社製、ポリトロン PT-350D 型)を用いて、回転数 16000sec<sup>-1</sup>で 10 分間剪断処理した。

#### [0049]

次いで、日立工機(株)製日立高速冷却遠心機 SCR20B 型(ローター:RPR9-2 型、回転半 径:170mm)を用いて、回転数 8000rpm で 60 分 間遠心分離を行い、上澄み液を回収した。

# [0050]

この粘土鉱物の乾燥物における純度、 ぐ電位及び粒径を表 1 に示す。

また、この粘土鉱物を実施例 1 と同様な方法で配合して調製した洗浄剤組成物の組成、増粘効果及び分散安定性を表 1 に示す。

# [0051]

# 実施例 4

5 リットルの純水に、塩化マグネシウム(純度 100%)を溶解し、MgO 換算 450ppm の水溶液を ppm was manufactured.

In this aqueous solution, 7 hours after stirring, approximately 15 hours standing it did supernatant which includes clay mineral of Working Example 1 (clay mineral 1.0 weight%) including 150 g.

After standing, centrifugal separation doing gel layer of clay mineral whichwas formed to bottom part of beaker, (350 rpm, 10 min) it recovered.

# [0047]

As for result of doing constituent analysis concerning clay mineral in gel which it acquires, 88 equivalent% of ion exchange property cation of clay mineral were substituted to Ca ion.

purity, ;ze electric potential and particle diameter in dried matter of this clay mineral are shown in Table 1.

In addition, combining this clay mineral with Working Example 1, and same method itshows composition, thickening effect and dispersion stability of detergent composition which it manufactures in Table 1.

# [0048]

#### Working Example 3

While Vanderbilt supplied saponite (DANA 71.3.1b.2) (tradename: beaker  $\triangle$  T, ignition remnant 85.3 wt%) stirring 118 g, in pure water 4882g, as clay mineral it added, 10 min shear it treated with rotation rate 16000 s<sup>-1</sup> furthermore making use of homogenizer (Cinema  $\overline{\tau}$  $\pi$ ) supplied. Polytron PT-350 D type).

# [0049]

Next, it did 60 min centrifugal separation with rotation rate 8000 rpm making use of Hitachi Koki Co. Ltd. (DB 69-053-6644) Ltd. make Hitachi high speed refrigerated centrifuge SCR20 B type (rotor:RPR9-type 2, radius:170 mm), supernatant recovered.

#### [0050]

purity, ;ze electric potential and particle diameter in dried matter of this clay mineral are shown in Table 1.

In addition, combining this clay mineral with Working Example 1, and same method itshows composition, thickening effect and dispersion stability of detergent composition which it manufactures in Table 1.

# [0051]

# Working Example 4

magnesium chloride (purity 100%) was melted in pure water of 5 liter, aqueous solution of the MgO conversion 450 ppm

# 調製した。

この水溶液に、実施例3の粘土鉱物を含む上澄 み液(粘土鉱物 1.0 重量%)150g を加え、7 時間 かきまぜたのち、約15 時間静置した。

静置後、ビーカーの底部に形成された粘土鉱物のゲル層を遠心分離(350rpm、10分)し、回収した。

得られたゲル中の粘土鉱物について組成分析 を行った結果、粘土鉱物のイオン交換性陽イオ ンの 95 当量%が Mg イオンに置換されていた。

# [0052]

この粘土鉱物の乾燥物における純度、 
を電位及び粒径を表 1 に示す。

また、この粘土鉱物を実施例 1 と同様な方法で配合して調製した洗浄剤組成物の組成、増粘効果及び分散安定性を表 1 に示す。

#### [0053]

#### 実施例 5

新潟県上石川産の酸性白土(固形分 91 重量%)350gを水 4650gに分散し、水酸化ナトリウム 30gを加えて、600 分撹拌した。

次いで、日立工機(株)製日立高速冷却遠心機 SCR20B 型(ローター:RPR9-2 型、回転半 径:170mm)を用いて、回転数 8000rpm で 60 分 間遠心分離を行い、上澄み液を回収した。

別に 5 リットルの純水に、塩化マグネシウム(純度 100%)を溶解し、MgO 換算 450ppmの水溶液を調製し、上記の上澄み液(粘土鉱物 1.0 重量%に調整)150g を加え、7 時間かきまぜたのち、約 15 時間静置した。

静置後、ビーカーの底部に形成された粘土鉱物のゲル層を遠心分離(350rpm、10分)し、回収した。

得られたゲル中の粘土鉱物について組成分析を行った結果、粘土鉱物のイオン交換性陽イオンの 97 当量%が Mg イオンに置換されていた。

# [0054]

この粘土鉱物の乾燥物における純度、ζ電位及び粒径を表 1 に示す。

#### was manufactured.

In this aqueous solution, 7 hours after stirring, approximately 15 hours standing it did supernatant which includes clay mineral of Working Example 3 (clay mineral 1.0 weight%) including 150 g.

After standing, centrifugal separation (350 rpm, 10 min) it did gel layer of clay mineral which was formed to bottom part of beaker, recovered.

As for result of doing constituent analysis concerning clay mineral in gel which it acquires, 95 equivalent% of ion exchange property cation of clay mineral were substituted to Mg ion.

# [0052]

purity, ;ze electric potential and particle diameter in dried matter of this clay mineral are shown in Table 1.

In addition, combining this clay mineral with Working Example 1, and same method itshows composition, thickening effect and dispersion stability of detergent composition which it manufactures in Table 1.

# [0053]

# Working Example 5

acidic clay of Niigata Prefecture Kamiishikawa product (solid component 91 weight%) it dispersed 350 g to water4650 g, 600 min it agitated including sodium hydroxide 30g.

Next, it did 60 min centrifugal separation with rotation rate 8000 rpm making use of Hitachi Koki Co. Ltd. (DB 69-053-6644) Ltd. make Hitachi high speed refrigerated centrifuge SCR20 B type (rotor:RPR9-type 2, radius:170 mm), supernatant recovered.

It melted magnesium chloride (purity 100%) in pure water of 5 liter, separately, manufactured aqueous solution of MgO conversion 450 ppm, 7 hours after stirring, approximately 15 hours standing it did above-mentioned supernatant (You adjust clay mineral 1.0 weight%) including 150 g.

After standing, centrifugal separation (350 rpm、10 min) it did gel layer of clay mineral which was formed to bottom part of beaker, recovered.

As for result of doing constituent analysis concerning clay mineral in gel which it acquires, 97 equivalent% of ion exchange property cation of clay mineral were substituted to Mg ion.

# [0054]

purity, ;ze electric potential and particle diameter in dried matter of this clay mineral are shown in Table 1.

また、この粘土鉱物を実施例 1 と同様な方法で配合して調製した洗浄剤組成物の組成、増粘効果及び分散安定性を表 2 に示す。

[0055]

比較例 1、

2

実施例 1 の山形県産のモンモリロナイト、実施 例 3 のバンダービルト社製サポナイトを使い、それぞれ配合した液体洗浄剤を調製した。

調製に際しては、この粘土鉱物 5 重量部を水 95 重量部に分散撹拌したのち、これとは別に AOS-Na(炭素数 14)2.5 重量%、LES-Na(炭素数 13、エチレンオキシド平均付加モル数 3)25.0 重量%、アミンオキシド 3.8 重量%を含む界面活性 剤水溶液 400 重量部を調製し、これに上記の 粘土鉱物分散液を撹拌しながら徐々に加えた。

得られた洗浄剤組成物の組成、増粘効果、分散安定性を、この粘土鉱物の純度、 
と電位、粒径とともに表 2 に示す。

[0056]

【表 1】

In addition, combining this clay mineral with Working Example 1, and same method itshows composition, thickening effect and dispersion stability of detergent composition which it manufactures in Table 2.

[0055]

Comparative Example 1,

2

montmorillonite of produced in Yamagata Prefecture of Working Example 1 (DANA 71.3.1a.2), Vanderbilt supplied saponite (DANA 71.3.1b.2) of Working Example 3 wasused, liquid detergent which is combined respectively was manufactured.

At time of manufacturing, while this clay mineral 5 parts by weight after dispersing agitating in water 95 parts by weight, separately from this AOS-Na (carbon number 14) 2.5 weight%, LES-Na (carbon number 13, ethylene oxide average number of moles added 3) manufacturing detergent aqueous solution 400 parts by weight which includes 25.0 weight%, amine oxide 3.8 weight%, agitating above-mentioned clay mineral dispersion in this it added gradually.

composition, thickening effect, dispersion stability of detergent composition which it acquires, purity, ;ze electric potential of this clay mineral, with particle diameter is shown in Table 2.

[0056]

[Table 1]

				実施例1	実施例2	実施例3	実施例 4
粘物	平均粒後 (nm)			280	350	450	500
土物	<b>で電位</b> (m V)			-60	- 3 5	-80	-35
鉱性	純度 (%)			98	98	98	9.8
洗	組	粘土鉱物		1. 0	1. 0	1. 5	1. 5
净	成	界	A O S - N a (R = 1 4)	2. 0	2. 0	_	-
剤		面	LAS-Na(R=12)	_	_	_	-
組	Î	活	LES-Na(R=13, p=3)	20.0	20.0	-	_
成	#	性	アミンオキシド	3. 0	3. 0	-	_
物	%	剤	POE (60) 硬化ヒマシ油	_	_	25.0	25.0
			活性剤計	25.0	25.0	25.0	25.0
	*		パランス	パランス	パランス	パランス	
	増料	幼男	艮(cP)	100	140	300	450
	分章	安定	2性	0	0	0	0

[0057]

[0057]

【表 2】

[Table 2]

				実施例5	比較例1	比較例2
粘物	平均粒径 (nm)			250	25000	45000
土物	<b>٢1</b>	位位	(m V)	-100	-25	- 1 0
鉱性	純度 (%)			99	8 5	8 5
洗	組	粘土鉱物		0.5	1. 0	1. 0
净	成	界	AOS-Na(R=14)	-	2.0	2. 0
剤		面	LAS-Na(R=12)	2. 0	_	-
組	Î	活	LES-Na(R=13, p=3)	8. 0	20.0	20.0
成	1	性	アミンオキシド	2. 0	3. 0	3. 0
物	%	剤	POE (60) 硬化ヒマシ油	_	_	_
			活性剤計	12.0	25.0	25.0
	水		パランス	パランス	パランス	
	增和	占効果	k (cP)	100	1 5	20
	分育	安定	往生	0	×	×

[0058]

[0058]

(注)

(Note)

AOS-Na(R=14):炭素数 14 の α -オレフィンスル

;al of AOS-Na (R=14 ):carbon number 14 -olefin sodium

Page 19 Paterra Instant MT Machine Translation

ホン酸ナトリウム

LAS-Na(R=12):炭素数 12 の直鎖状アルキルベンゼンスルホン酸ナトリウム

LES-Na(R=13、p=3):エチレンオキシド平均付加 モル数 3 のポリオキシエチレンアルキル( $C_{13}$ )エ ーテル硫酸ナトリウム

アミンオキシド:ラウリルジメチルアミンオキシド

POE(60)硬化ヒマシ油:エチレンオキシド平均付加モル数 60 のポリオキシエチレン硬化ヒマシ油

sulfonate

straight chain sodium alkylbenzene sulfonate of LAS-Na (R=12 ):carbon number 12

polyoxyethylene alkyl ( $C_{13}$ ) ether sodium sulfate of LES-Na (R=13, p=3):ethylene oxide average number of moles added 3

amine oxide: lauryl dimethyl amine oxide

polyoxyethylene hydrogenated castor oil of POE (60) hydrogenated castor oil: ethylene oxide average number of moles added 60